

THE IDENTIFICATION AND CHEMISTRY OF SPECIES RESULTING FROM
THE RAPID PYROLYSIS OF SMALL COAL PARTICLES IN VACUUM
AND IN THE PRESENCE OF REACTIVE GASES

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INTRODUCTION

The various experiments in this study are designed to produce data from reactors which emphasize the early stages of coal gasification and its reactions with auxiliary gases by bringing the coal quickly up to reaction temperature under conditions where highly reactive gas phase intermediates can exit rapidly from the reaction zone. They are then deposited on a 15K reflective surface with a large excess of inert gas where further reaction is rapidly quenched. The products when isolated in a non-interactive solid such as nitrogen, argon, or even dry air exhibit well-defined spectra which allow the precise measurement of isotopic shifts and peak positions. Free radicals and other reactive species can be detected by characteristic infrared spectra. The presence of intermediates is also monitored with a fast time response quadrupole mass spectrometer. The combination of mass spectrometry and matrix isolation infrared spectroscopy serves as an effective probe for the existence of transient gaseous reaction intermediates.

The types of data obtained from the studies include:

- (1) Structural data for new species and suggested reaction pathways from isotopically-substituted reactants.
- (2) Information on the dependence of various gas products formed on rates of heating, reactant gases, and coal particle size.

The question as to whether the reactions of particular primary building blocks of coal lead to specific products is studied by adding the molecular species, i.e., various polycyclic aromatics (PCA's) to the coal or as a reactant gas and noting the effect on product distribution.

EXPERIMENTAL

A new matrix isolation system has been designed to allow both mass spectrometric and matrix isolation infrared studies of highly reactive transient species. Close coupling with differentially pumped systems permits the detection of species evolving from samples exposed to pressure pulses of various gases up to one atmosphere. The system is integrated into a high resolution Fourier transform spectrometer which covers the spectral range from the far i.r. to the near i.r. (100 microns to 1 micron). The design has seventy available deposition surfaces. This large number of surfaces is very valuable in attempts to detect small changes which occur due to changed reactor conditions. The increased accuracy of infrared difference spectroscopy can be used to great advantage with a large number of samples which result from small changes in reactor conditions. The combination of mass spectrometric and matrix isolation spectra greatly increase the likelihood of positive species identification. Three quartz crystal

infrared. Results from this study are presented in Figure 5.

At 146C, coal devolatilization can be characterized by evolution of CO_2 , CH_4 , H_2O , and CO . At an increased temperature of 326C, light hydrocarbon gases such as C_2H_4 and C_2H_6 are observed along with CH_4 , CO_2 , CO and H_2O . Most of these light hydrocarbons are devolatilized between 326 and 605C. A similar behavior has been noted by Solomon and co-workers. /1,2/ At 1038C, a new peak at 1525 cm^{-1} appears which has not yet been identified.

An interesting observation is that CO_2 seems to reach maximum yield at low temperatures and remains relatively constant at higher temperatures. However, CO appears to increase with higher temperatures and does not reach a maximum at the highest temperature studied.

Rapid Pyrolysis of Illinois #6

Studies of rapid pyrolysis of coal granules, using the pulsed flow reactor and the coal granule inlet valve described in Figure 3 indicate results similar to those for slow pyrolysis. However, rapid pyrolysis of Illinois #6 powder gives a much more complex IR spectrum with two new peaks appearing at 1180 and 1328 cm^{-1} . These two peaks are predominant and always occur simultaneously. Their relative intensities are always the same, indicating that they are due to a single species.

A comparison of rapid pyrolysis of Illinois #6 granules versus powders is illustrated in Figure 6.

Two other coals beside Illinois #6 were studied, Western Kentucky and Upper Freeport as shown in Figure 7. Western Kentucky is a high moisture and high oxygen content coal while Upper Freeport is a low moisture and low oxygen content coal. Both types of coal gives results similar to Illinois #6 when their powders are rapidly pyrolyzed. Absorptions at 1180 and 1328 cm^{-1} are predominant over the methane absorption for both coals studied. This indicates that the species responsible for 1180 and 1328 cm^{-1} is common to all coals during rapid pyrolysis.

Rapid Pyrolysis of Oxidized Illinois #6

Illinois #6 powder was oxidized by heating in an oven at 190C. Samples taken after one hour and after 18 hours of heating were rapidly pyrolyzed through the pulsed flow reactor. Figure 8 shows the predominant gaseous products to be CO_2 , CO and H_2O , as expected for oxidized coal. Slight traces of CH_4 and the species responsible for 1180 and 1328 cm^{-1} are also observed. This indicates that the presence of the unidentified intermediate species is not dependent upon the extent of oxidation of the coal samples. It is, however, reduced in yield which indicates the species is not due to oxidation of the coal sample.

Rapid Pyrolysis of Illinois #6 with D2016 and D2018

The effect of gaseous water on rapid pyrolysis of Illinois #6 granules was studied by the addition of D2016 and D2018. Gaseous deuterated water was pre-mixed with argon and pulsed through the reactor immediately after coal granules were dropped into the hot reactor zone. Results, shown in Figure 9, suggest that oxygen from

mass monitors are mounted on the cold trapping block. They serve as very sensitive quantitative monitors of the beam density striking the trapping surface. A detailed schematic of the MI-MS apparatus is shown in Figures 1 and 2.

Figure 3 presents a schematic diagram of a pulsed flow reactor for coal granules and coal powders. The reactor contains three sections. The first section, A, contains the coal granule inlet valve. The second section, B, contains the hot reactor zone, resistively heated through a nichrome wire wrapped around the outside of the quartz tube. It is separated from the cold (15K) copper matrix isolation surface by a small amount of quartz wool inserted in the tube. Coal granules are introduced into the hot reactor zone by simply dropping them in through valve A. A two-way valve is then pulsed open which causes an inert gas, argon, to carry the gaseous products through the quartz wool and onto the 15K copper surface of the matrix isolation apparatus. Approximately 15 grains of coal were used for each trapping.

The third section, C, is used for introduction of coal powders into the hot reactor zone. It contains a fluted glass column, separated from the hot reactor zone by two two-way valves. The inert carrier gas, argon, is let in from the bottom, passing the frit, creating a simulated fluidized bed of coal powder. Coal powder along with the inert gas is pulsed into the hot reactor zone by sequentially pulsing open each of the two-way valves. Gaseous products are carried by the excess inert gas onto the 15K matrix isolation surface to be studied by infrared spectroscopy. Usually 50-100 pauses of coal powder were used for each trapping.

PULSED FLOW VERTICAL HEATER REACTOR

A schematic drawing of the vertical heater reactor is shown in Figure 4. This reactor is very similar to the pulsed flow reactor described in Figure 3, except that the design allows the gaseous products to be trapped directly onto the matrix surface without formation of tars along the sides of the tube as in the case for the previous reactor. The hot reactor zone is placed in the matrix isolation chamber. It consists of a quartz tube with a small opening near the bottom of the tube which is inserted into a vertical tantalum heater. The tantalum heater also has a small opening on the side facing the matrix isolation surface. A small piece of quartz wool is placed into the quartz tube so that it just covers the opening. This prevents particles from being blown onto the matrix surface and keeps them in the hot reactor zone.

Coal powder is pulsed into the heater in the same way as described for the previous pulsed flow reactor. In general, pyrolysis is carried out over a temperature range of 120 to 1000 C, in vacuo. Argon has been used as the inert carrier and matrix gas.

RESULTS

Slow Pyrolysis of Illinois #6 Powder

Coal particles (250 mesh) are placed in the vertical quartz tube described in Figure 4 and slowly heated from 146C to 1038C. Gaseous products obtained at different intervals of temperature are trapped with argon, introduced from a separate inlet tube, onto the 15K copper matrix isolation surface and subsequently examined through

the water ends up as CO and CO₂, as seen by the presence of CO18 and CO16O18 in the reaction with D2O18. However, no deuterated methane is evident in either reactions.

DISCUSSION

To date our work has shown that the product gaseous species from pyrolysis are very dependent on coal particle size. As might be expected, the larger particles tend to produce the smaller alkanes and alkenes as a result of secondary pyrolysis. Rapid pyrolysis of the smaller particles produces new species which are thought to be more representative of the species resulting from initial bond breaking steps. One species in particular produces strong features at 1328 and 1180 cm⁻¹. Insufficient reference data has prevented the identification of this species as yet but it is hoped that studies of model compounds and additional mass spectrometric information will allow identification of this significant reaction intermediate. It is also clear that improved control of particle size and the amount of coal injected per pulse will greatly aid our interpretation of product distributions. Of course, this also applies to studies of reactions with gases such as water, hydrogen and carbon dioxide. Preliminary work with a small gas recirculating system in which selected coal particle sizes are entrained with reactant and inert gases indicates that a much improved pulsed coal injection system is possible. It is expected that considerable additional data of product distributions correlated to particle size, temperature and reactant gas will be available in the near future.

REFERENCES

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2. Adv. in Chem. Series, 192, Coal Structure, Ed. M.L. Gorbaty and K. Ouchi, Chap. 7, "Coal Structure and Thermal Decomposition", P.R. Solomon.

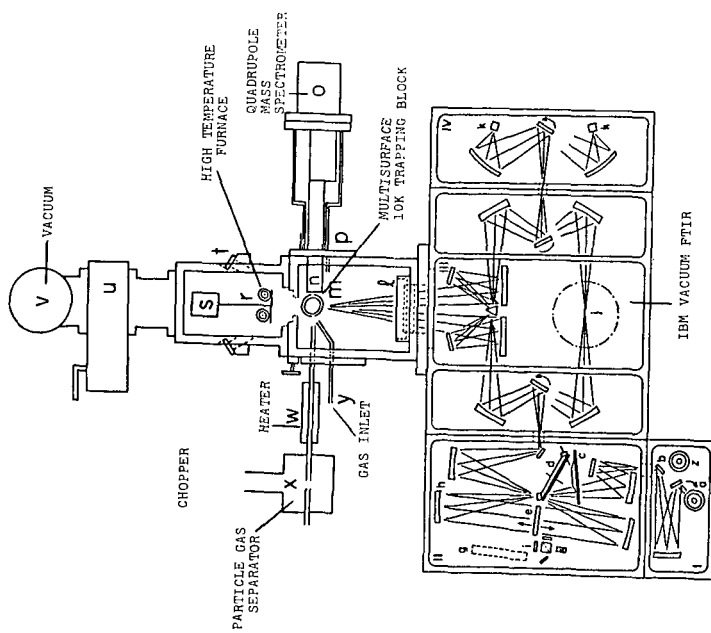


FIGURE 1

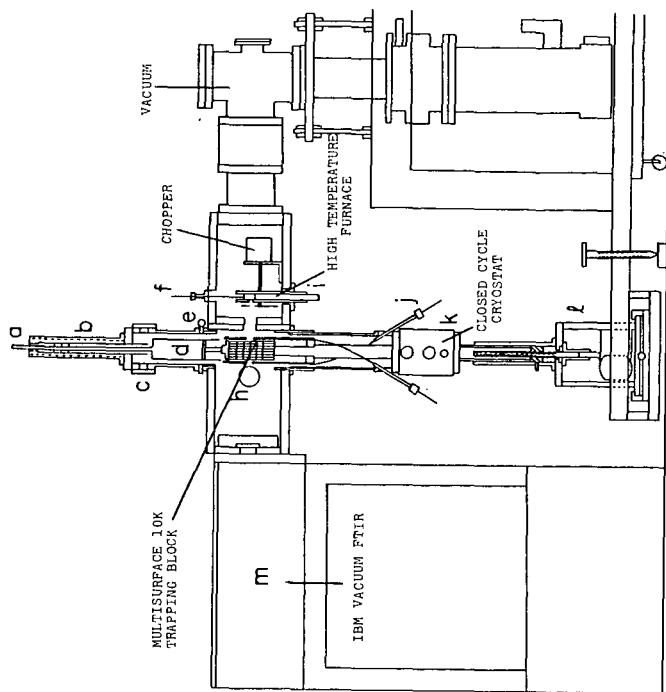


FIGURE 2

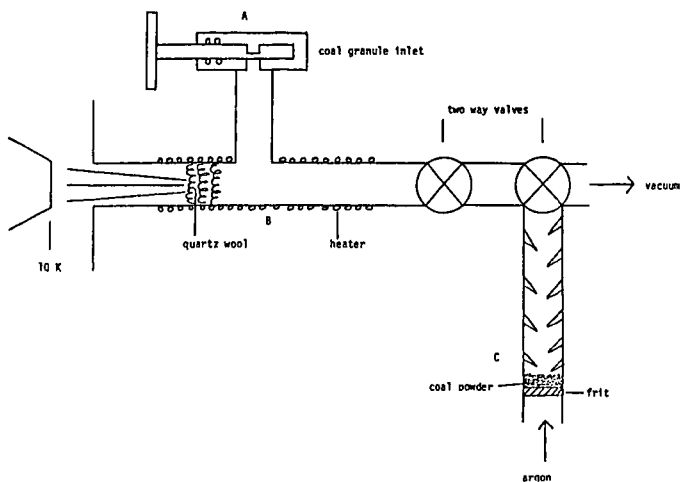


Fig. 3. PULSED FLOW REACTOR

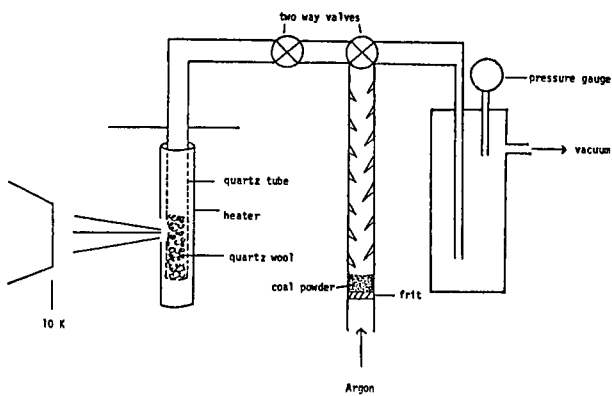


Fig. 4. PULSED FLOW VERTICAL HEATER REACTOR

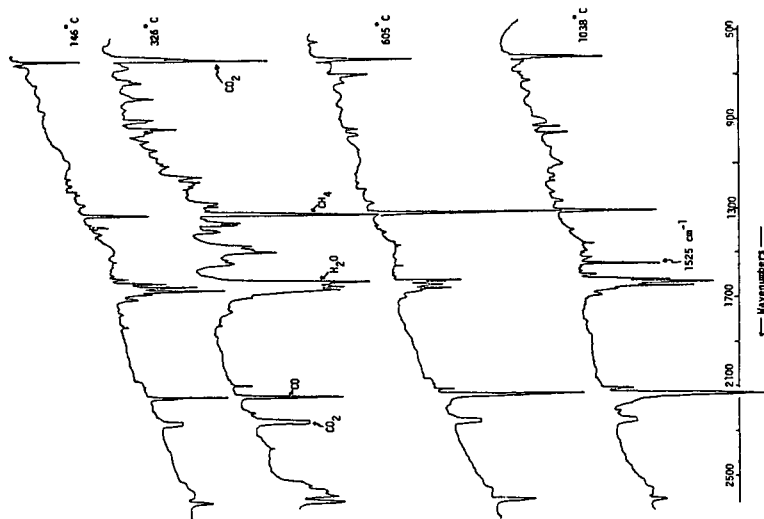


Fig. 5. Slow Pyrolysis of Illinois #6 Powder

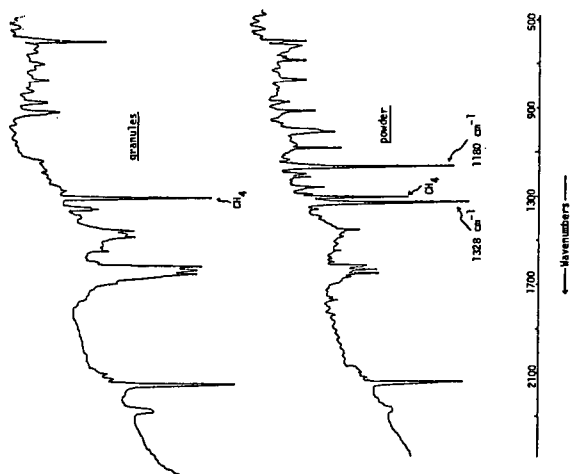


Fig. 6. Rapid Pyrolysis of Ill. #6 at -1000°C

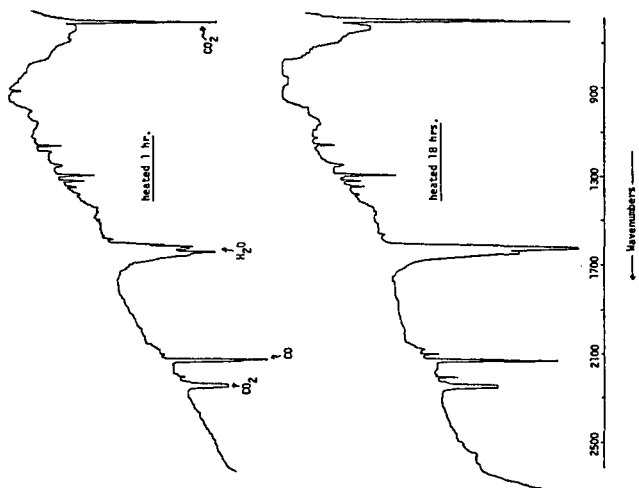


Fig. 8. Rapid Pyrolysis of Oxidized J11. #6

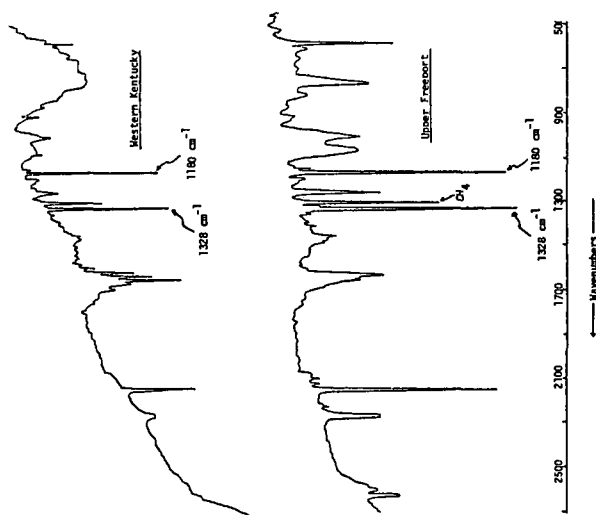


Fig. 7. Rapid Pyrolysis of Other Coals at 1000°C

Fig. 9. Rapid Pyrolysis of Ill. #6 with D_2O^{16} & D_2O^{18}

